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Preparation and Characterization of ZnO NWs/Graphene Nanocomposite as an Effective Photoanode Electrode for Improving the Performance of the Dye-Sensitized Solar Cells

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***Abstract*—The present study, fabricated DSSCs using pure ZnO NWs and ZnO NWs/Graphene nanocomposite as photoelectrodes. Graphene was incorporated into pure ZnO NWs through a cost-effective Hydrothermal Process to act as an electrical charge carrier. J-V curve of prepared nanocomposite was recorded with a light intensity of 100 mW.cm^{-2}. The created nanocomposites were thoroughly investigated by using different electrical and structural characterization techniques such as SEM, XRD, and J-V characteristics. According to SEM examination, the ZnO NWs/graphene composite-based electrode has more porosity than the electrode made using pure ZnO NWs, increasing the surface area and the amount of dye that can be absorbed. From the graphene advantages ,the reduced internal resistance and electron recombination loss, these properties allow electrons to transfer to the collection electrode efficiently. Based on these benefits, the ZnO NWs/Graphene nanocomposite photoanode with a thickness of 965.11 nm that was used in the DSSC2 was demonstrated a J_{sc} of 19.50 mA.cm^{-2} and conversion efficiency of 9.829053%, which opposite to the result of the DSSC1 without graphene. These results can be encouraged for future improved optoelectronic devices.**

Keywords: ZnO NWs, Graphene, Nanocomposite, Hydrothermal, and DSSCs.

I. Introduction

Today, solar electricity is a rapidly expanding energy source, and solar cells have found use in everything from large-scale power plants to small-scale electronic products. There is great potential for dye-sensitized solar cells (DSSCs) to replace conventional p-n junction solar cells at a lower cost[1][2]. DSSCs are the most promising next-generation photovoltaic systems due to the contributions of a number of advantages, including low cost, good quantum conversion efficiency, simple device fabrication, lightweight, ability to operate in diffuse sunlight as well as wide-angle variations, and adjustable artistic features like transparency and color[3][4]. The light-harvesting efficiency, charge transport, and charge recombination rate greatly influence the power conversion efficiency (PCE) of DSSCs. These parameters directly impact the morphology and structure of photoanode materials[5]. A DSSC device consists comprises a mesoporous nanocrystallite photoanode film (often constructed of TiO_2 or ZnO) with a monolayer of the sensitizer dye surrounding its outer surface, an electrolyte with an iodide/tri-iodide redox pair (I^-/I^{-3}), and a counter electrode (Pt-coated FTO CE)[6]. However, the increased additional conversion efficiency has been constrained by energy loss brought on by recombination between electrons and either the oxidized dye molecules or electron-accepting species in the electrolyte during the charge transfer process[7][3].

Such recombination is primarily caused by the absence of a depletion layer on the TiO_2 nanocrystallite surface and gets much worse as the photoelectrode film thickness rises. This has been thoroughly investigated using DSSC technology based on ZnO. ZnO is a possible substitute for TiO_2 in the production of DSSC photo-anodes[8][9]. As a photoanode, zinc oxide (ZnO) semiconductor is crucial for enhancing the conducting interface layer and the effectiveness of (PCE). At room temperature, ZnO has a substantial exciton binding energy of 60mV, and a wide bandgap (3.37 eV), However, its electron mobility is 2-3 orders of magnitude higher[10]. Functional nanostructured photoelectrodes like nanowires have undergone extensive investigation and are projected to significantly increase the electron diffusion length in the photoelectrode films by providing a direct conduction pathway for the fast collection of photogenerated electrons. By substituting the typical TiO_2 random polycrystalline nanoparticle network with ordered crystalline ZnO semiconductor nanowires (NWs), the potential of charge

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recombination during antiparticle percolation would be reduced[11]. Metal oxides and carbon allotropes are two of the most sought-after materials in the field of materials science due to their synergistic relationship with other elements that are required for technological applications in a variety of fields. Nanocomposites made of two or more materials with desired performance have recently become one of the most explored areas. In the family of metal oxides, ZnO is the functional material that has been studied the most[12][13]. One of the carbon allotropes is graphene, a 2D sheet comprised of carbon atoms arranged in a one-atom-thick hexagonal lattice. It has a large surface area of 2,600 m^2 g^{-1}, high thermal conductivity, high electrical conductivity, and high carrier mobility (Theoretical prediction)[14]. Thus, ZnO/graphene nanocomposite is anticipated to display exceptional features in applications such as photocatalytic activity, energy storage, optoelectronics, and solar energy conversion[15].

This study can be divided into two parts. Firstly, pure ZnO NWs as photoanode were studied to investigate the characteristic and PCE properties of DSSC1. Secondly, the composite has been synthesized ZnO NWs/graphene by hydrothermal method to act as charge carriers. The doctor blade method was employed to deposit ZnO NWs/graphene on conductive glass substrates as a photoanode electrode in DSSC2. The photovoltaic performance of a DSSC based on a ZnO NWs/graphene composite photoanode was compared to pure ZnO NWs. The cells were constructed using an iodide-based electrolyte, a platinum (Pt) plated FTO as a counter electrode (CE), and N719 dye as a sensitizer. The constructed cells' morphological, structural, compositional, and J-V properties were investigated.

II. Experimental Section

A. Synthesis of ZnO NWs/Graphene Films as Photoanode

Hydrothermal Process prepared ZnO NWs/graphene nanocomposite photoanodes. Typically, pure ZnO NWs 1g and graphene 0.025g were dissolved in 10 ml of ethanol and 50 ml of deionized water, then mixed for 1 h at room temperature using an ultrasonic mixture. The resulting solution was then added to an autoclave, and heated to 120 C° for 48 h. The resulting solution was centrifuged after the allotted time, and the precipitate (ZnO NWs/graphene wet powder) was then washed with ethanol before being rewashed again with water. Finally, it was dried in a hot oven at 50 C° for 4 h. Preparation of the paste ZnO NWs/graphene composite paste was prepared by adding 0.5 g ZnO NWs/graphene in 10 ml ethanol for 1 h. The abovementioned solution was kept on a continuous magnetic stirrer, and 0.5 g of ethyl cellulose, a few drops of terpinol, and 0.5 ml of acetylacetone were added to it as a pore-filling agent. In order to create ZnO NWs/graphene thin films, a paste was dropped on top of FTO glass (1 cm × 1 cm) and spun at 6000 rpm for 1 min by using a device (China, Model NO.CY-100B). Following drying, the samples were annealed for 4 h at 450 C° before being allowed to cool naturally.

B. *Fabrication of DSSCs devices*

Ruthenium (N719) dye 1g and 50 ml of ethanol were added to the surface-treated ZnO NWs/graphene films to fabricate DSSCs, which were then left in the solution for 24 h at room temperature. Platinum (pt $_{film}$) coated FTO glass (prepared in a Thermal Evaporation in Vacuum method (TEV)[16]) was used as the counter electrode. The DSSC was sandwiched between the ZnO NWs/graphene film-coated FTO glass (anode) ,and the pt film coated onto FTO glass (cathode), The final step after injecting electrolyte (I^-/I^{-3}) between two electrodes of the DSSCs was to expose the solar cells to light at a 100 $mW.cm^{-2}$ intensity.

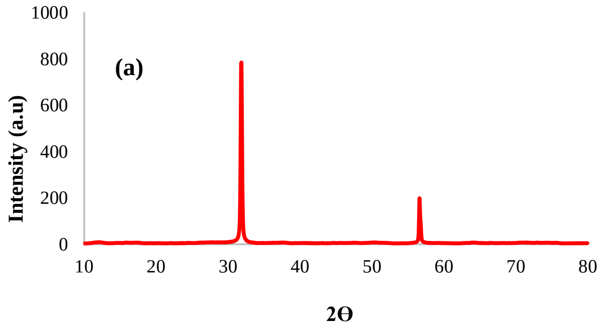
C. Characterization Tools

SEM to check the surface morphology of the composite material, and XRD to get the crystal structure, crystalline size, and another detailed study of optical, morphological, and structural properties. The surface morphology was investigated using the SEM of the ZnO NWs/graphene composite-based electrode by using (Czech Republic, TESCAN, and MIRA III). Structural properties of the ZnO NWs and ZnO NWs/graphene composite-based electrodes were carried out utilizing an XRD to look into the crystal structure, crystallite size, and crystal orientation, model (Netherland, PHILIPS, PW1730, and wavelength: 1.54056A°). The photovoltaic performance of DSSC1 and DSSC2 were studied su as V_{oc}, and J_{sc}, by utilizing a solar simulator and a Keithley 2400 source meter (ENLITECH Model SS-F5-3A). Then, the FF and efficiency (Ƞ).

III. Results and Discussion

A. Structural Properties

Figure 1(a) depicts the pure ZnO NWs' X-ray diffraction pattern. The diffraction two peaks at 31.737° and 56.536°, which are indexed to the wurtzite structure of ZnO NWs, correspond to the (010) and (110) planes, respectively. [17]. The observed planes agree with the common JCPDS data file (Card No. 89-0510). Additionally, the ZnO NWs/graphene nanocomposite exhibits comparable planes that correlate to the ZnO wurtzite structure, as illustrated in Figure 1(b). A faint broad peak at 26.668° is due to the distinctive peak of graphene in addition to the ZnO diffraction peaks. The absence of graphene peaks showed that the synthesis process had finished reducing graphene[18][19] and confirmed the formation of ZnO NWs/graphene nanocomposite.



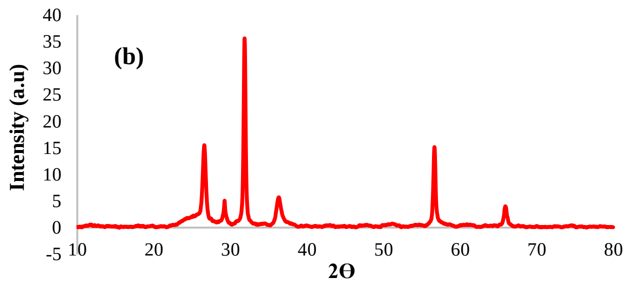
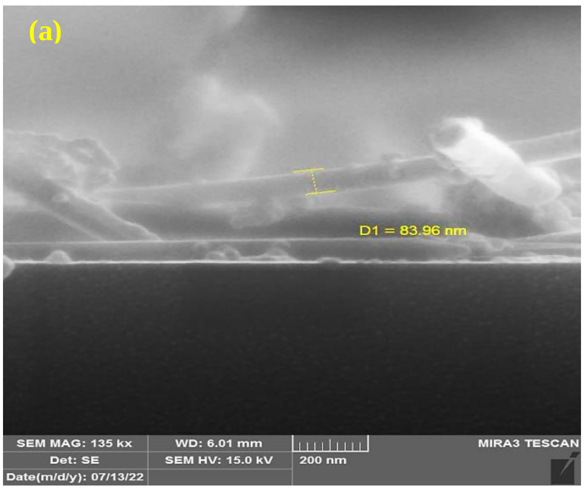
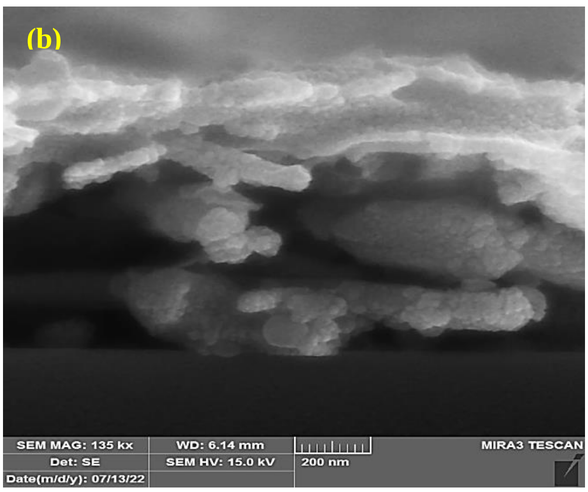


Figure (1): (a) XRD pattern of the synthesized pure ZnO NWs, and (b) ZnO NWs/graphene nanocomposite.

B. Morphological Properties

Using SEM images, the surface morphology of prepared samples was examined. The SEM images of prepared ZnO NWs and ZnO NWs/graphene nanocomposite films are shown in (Figure 2a, b, and c). Figure 2(a) shows that these films have porous and rough morphology, as well as wire-like structures made of ZnO NWs, the average cross-section of a single nanowire was shown to be ~83.96 nm (Figure 2a).





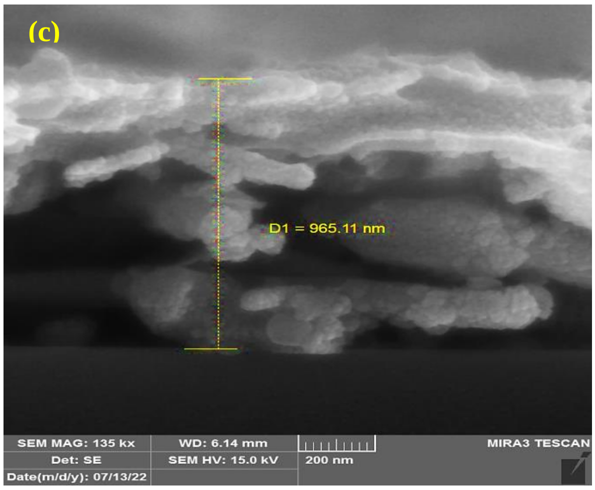


Figure (2): SEM images of (a) The average cross-section of a single nanowire, (b) ZnO NWs/graphene composite, and (c) The thickness of photoanode films.

SEM results further demonstrate the production of ZnO NWs/graphene composite structures, and graphene nanosheets have been effectively loaded onto pure ZnO NWs, it is observed from the SEM analysis, shows as compared to an electrode fabricated of pure ZnO NWs, the ZnO NWs/graphene nanocomposite electrode had a larger porosity and the greater surface area created by increased porosity would allow for greater dye absorption (Figure 2b). That the thickness (~965.11 nm) of both photoanode films is almost the same and is firmly attached to substrates of FTO glass (Figure 2c).

C. *Performance Analysis of Cells*

Table (1) shows the photovoltaic performance of the manufactured DSSCs, and Figure (3) shows the related J-V characteristics.

Table (1): Shows the photovoltaic performance of photoanode electrodes from J–V curves.

Photoanode	**Dye**	**CE**	**J_{sc} (mA.cm^{-2})**	**V_{oc} (V)**	**FF (%)**	**Efficiency (%)**
Pure ZnO NWs	N719	Pt film	19.05	0.681	0.732	9.49627
ZnO NWs/Graphene	N719	Pt film	19.50	0.683	0.738	9.82905

According to the current study, that photoanodes electrode shape impacts cell's performance, so it must be improved to raise the DSSCs photoconversion efficiency. Compared to a pure ZnO NWs-based DSSC1, the DSSC2 with graphene as the photoanode performs better. Because of the grain boundaries in nanowires that prevent fast electron transport, the low efficiency of DSSC1 is caused by a rise in the recombination of electrons with an electrolyte. The use of graphene increases a thin film's conductivity and facilitates electron transport through the photoelectric cell. In addition, ZnO NWs containing graphene offer greater conductivity than pure ZnO NWs, leading to higher J_{sc}.

Higher J_{sc} (19.50 mA.cm^{-2}) for the manufactured DSSC2 results from the longer ZnO NWs/graphene composite photoanode providing a stronger conductive channel for the transmission of electrons. Higher V_{oc} (0.683 V) and conversion efficiency (9.829053%) are also displayed by the same cell. In light of the above, we could benefit from adding graphene to facilitate quick electron transport within the photoanodes.

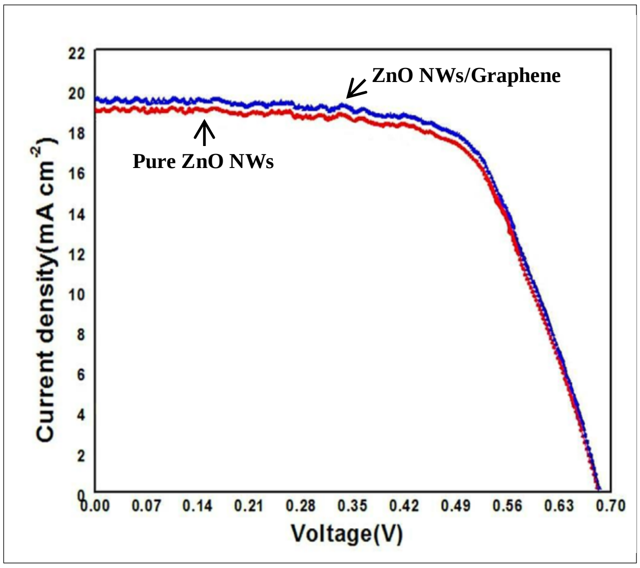


Figure (3): J–V characteristics of DSSCs fabricated using pure ZnO NWs and ZnO NWs/graphene nanocomposite electrodes

IV. Conclusion

In conclusion, by using a spin coating to create pure ZnO NWs and ZnO NWs/graphene thin films as photoanodes, has successfully manufactured two DSSCs devices. The maximum efficiency of the DSSC2 device was 9.829053 % at an annealing temperature of 450C°. It was discovered that photoanode materials' shape impacts how efficient devices are. This research reveals how the DSSCs device's efficiency is significantly impacted by adding graphene to the photoanode. To increase the efficiency of DSSCs, the photoanode electrode, which is a crucial component of solar cell performance, must be tuned. As a result, the ZnO NWs/graphene nanocomposite could serve as an alternate type of photoanode for effective third-generation DSSCs.

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